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(54) Metal-coating compositions
and preparative methods and uses
for such compositions

(57) Metal-coating compositions for
use in so-called "no waste" pre-
treatments designed to secure maxi-
mum corrosion-protection consistent
with good paint-adhesion properties
achieve increased "universality"
under different paint systems are
formulated from (a) mixed Cr com-
pounds consisting of Cr⁶⁺ and
Cr³⁺, the Cr³⁺ formed by reducing
40-60% of Cr⁶⁺ (b) phosphoric
acid, (c) polyacrylic acid and (d)
acrylic emulsion polymer, and (e)
sufficient water to form a solution-
like composition. The compositions
are used in various processes for
coating metals such as iron, zinc
and aluminium.

Does not convert?

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SPECIFICATION

Metal-coating compositions and preparative methods for such compositions

- 5 This invention concerns metal-coating compositions and preparative methods and uses for such compositions. More specifically the invention relates to chrome-based compositions for coating the metals commonly used in industrial practice, above all iron, zinc and aluminium, so as to improve their corrosion-resistance and paint-adhesion properties, and thus to prepare them to receive a subsequent siccative finish, as well as to methods of preparing such chrome-based
- 10 metal-coating compositions and processes using such compositions for applying coatings to such metals.
- The terms "iron", "zinc" and "aluminium" are all used herein to mean not only the respective pure metals but also alloys thereof in which the named metal is the predominant ingredient; and the term "zinc" moreover also includes galvanized or otherwise zinc-coated iron.
- 15 Many different treatments have been proposed for improving the corrosion-resistance and paint-adhesion properties of metals, for instance those in which a chemical conversion coating is formed upon the metal surface by treatment thereof with aqueous acid phosphate or acid chromate solutions, including procedures in which resinous vehicles are added to aqueous chromic acid treating solutions. Whatever the particular system employed, the ultimate objective
- 20 of all such practices is always essentially the same, namely to secure the maximum possible protection of the metal substrate against corrosion consistent with simultaneously achieving high levels of impact-resistance, flexibility and paint-bonding qualities. The very proliferation of proposals for securing such a desirable combination of properties shows how difficult that may often be to achieve in industrial practice.
- 25 Nor are the corrosion-resistance and paint-bonding properties of the coating itself the only important attributes of any such metal-treating method. It is also highly desirable to be able to employ a metal-coating system in which the coating is formed simply by contact with the metal surface followed by drying (usually hot-air drying or oven-baking) and thus without any need to remove excess coating material from the surface by rinsing or squeegeeing, because such
- 30 treatments—usually referred to as "no waste" pretreatments—have obvious ecological benefits due to the fact that effluents—toxic or otherwise—are not evolved in the course of the treatment.
- There are already-available "no-waste" pretreatments which have much to commend them, but unfortunately they lack "universality" with respect to the paint systems that can subse-
- 35 quently be applied to the thus-treated metal surface. No single "no waste" metal pretreatment is yet known that will give optimum performance under a wide variety of different paint systems, and thus "no waste" pretreatments that give optimum performance under a solvent-type paint system may not give comparable results under water-base type paint systems, and vice versa. Indeed even as between different types of solvent-paint systems (such as polyester,
- 40 vinyl, alkyd, plastisol and organosol paint systems) optimum performance cannot be guaranteed using the same "no waste" pretreatment. Accordingly known "no waste" pretreatments whatever their other merits may require adaptation to the particular use envisaged—and in effect must in practice be specially-tailored to meet the needs of the particular paint system under which it will be used.
- 45 One of the most satisfactory of the known "no waste" pretreatments is that described in Schiffman's United States Patent No. 3,185,596; but even so, that metal-coating pretreatment, though it performs excellently when used under vinyl paints, has been found to be simply ineffective when used under polyester paint systems.
- We however have now found that the "no waste" pretreatment formulations broadly-disclosed
- 50 in Schiffman's United States Patent No. 3,185,596 can be modified and extended in such a way that while still imparting outstanding corrosion-resistance to the surfaces of metals such as iron, aluminium and zinc they acquire greater "universality"—specifically being then useful under both vinyl and polyester paint systems, and indeed so far as we have ascertained also under many other types of paints and paint systems.
- 55 Schiffman's United States Patent No. 3,185,596 is concerned with metal-coating solutions that contain "mixed chromium compounds" together with water-soluble or water-dispersible polyacrylic acid. These so-called "mixed chromium compounds" are mixtures of hexavalent chromium and trivalent chromium compounds which can be prepared by partially-reducing aqueous acid solutions of hexavalent chromium, using any of many known techniques to effect
- 60 the reduction, and preferably such reducing agents as do not form objectionable reaction products which will be retained in the treating solution. Specifically the Schiffman United States Patent No. 3,185,596 prefers formaldehyde for use as the reducing agent to effect the partial reduction, as is more fully described in Schiffman's earlier United States Patent No. 3,063,877, and employs it to effect reduction of from at least 20% to about 60% of the hexavalent
- 65 chromium. The earlier Schiffman United States Patent No. 3,063,877 points out that solutions

- containing such values of partially-reduced chromium can be used to improve the corrosion-resistance of not only a previously-applied coating but also the surface of a metal substrate. The later Schiffman United States Patent No. 3,185,596 discloses that an aqueous solution containing at least 0.25% by weight of the aforementioned mixed chromium compounds can be
- 5 made to yield a coating, when applied to metal substrates, which has greatly improved corrosion- and impact-resistance, flexibility and paint-bonding properties by adding thereto at least 0.25% by weight of a polyacrylic acid compound. These polyacrylic acid compounds could be of either the water-soluble or the water-dispersible type. Specifically there mentioned are the water-soluble types of polyacrylic acid compounds which are readily available as standard
- 10 articles of commerce from Rohm & Haas Company, including those known under the trade name Acrysol, for example the aqueous solutions of polyacrylic acids having different molecular weights and viscosities sold as Acrysol A-1 and Acrysol A-3. Also disclosed there as suitable for use is the water-dispersible emulsion of polyacrylic acid which is commercially available and known as Rhoplex AC-200.
- 15 In order to achieve the objectives of the present invention, namely the formation by a "no waste" pretreatment of resinous, protective, flexible and impact-resistant paint-bonding coatings upon the surfaces of iron, zinc, aluminium and perhaps other metals which coatings exhibit high performance when used under a number of different types of paints and paint systems, we employ compositions which essentially must contain a blend of hexavalent chromium, trivalent chromium, phosphoric acid, soluble polyacrylic acid and water-dispersible acrylic emulsion
- 20 polymer, at least some and very desirably all of these essential ingredients being moreover present in certain specific ratios.
- As compared with the previously-discussed Schiffman United States Patents Nos. 3,185,596 and 3,063,877, there are however important differences which must be observed if the
- 25 advance offered by the present invention is to be achieved.
- Perhaps most importantly, it is necessary that the degree of partial reduction of the hexavalent chromium shall be such that the proportion of hexavalent chromium reduced to the trivalent state shall be in the range of from 40% to 60%; and indeed we strongly recommend that this proportion should be kept below 55% and very desirably within much narrower limits of 46%
- 30 to 50%, for reasons which will be explained subsequently.
- Almost equally important is the fact that phosphoric acid is not optional but must be present, and very desirably should be present in a ratio by weight of from 3 to 4 parts of phosphoric acid (100% H_3PO_4) per 10 parts of the mixed chromium compounds, for reasons which will be explained subsequently.
- 35 It is also essential that the composition of this invention should contain water-soluble polyacrylic acid, and if not quite essential it certainly is highly important that the composition should contain a much lower proportionate concentration of water-soluble polyacrylic acid than that disclosed in Schiffman's United States Patent No. 3,185,596, namely a ratio by weight of from 4 to 5 parts of polyacrylic acid solids per 10 parts of the mixed chromium compounds, for
- 40 reasons which will be explained subsequently.
- Still further it is moreover essential that the compositions of this invention should contain acrylic emulsion polymer, and if not quite essential it certainly is highly important that they should contain a rather large proportionate concentration of acrylic emulsion polymer, namely a ratio by weight of from 17 to 20 parts thereof per 10 parts of the mixed chromium compounds,
- 45 for reasons which will be explained subsequently.
- According to one aspect of this invention there is therefore provided an aqueous metal-coating composition for coating metal surfaces to enhance their corrosion-resistance and paint-adhesion properties, which comprises:
- (a) mixed chromium compounds consisting of a mixture of hexavalent chromium and trivalent chromium formed by reducing from 40% to 60% of the hexavalent chromium to the trivalent
- 50 state; together with
- (b) phosphoric acid;
- (c) polyacrylic acid;
- (d) acrylic emulsion polymer; and
- 55 (e) water in an amount at least sufficient to dissolve and/or disperse all the other components therein to form a solution-like composition.
- While some of the benefits of this invention can be achieved when the proportion of hexavalent chromium reduced to the trivalent state is within the above-specified 40%-60% range, there is some sacrifice of the stability of the composition towards the upper end of that range, and we therefore strongly recommend that this proportion should not exceed 55%.
- 60 Towards the lower end of the range there is moreover some sacrifice of the paint-adhesion properties of the coatings formed by the composition, and accordingly so as to secure an optimum balance between the stability of the composition and the paint-bonding properties of the resultant coatings, and moreover to achieve the widest possible "universality" under
- 65 different paints, we greatly prefer that proportion of hexavalent chromium reduced to the

trivalent state should be kept within the narrow range of from 46% to 50%.

Phosphoric acid must be present because it has a decided and generally beneficial influence upon both the corrosion-resistance and the paint-adhesion properties of the coatings formed by the compositions. The proportion of phosphoric acid present relative to the mixed chromium compounds seems however to influence the paint-adhesion properties of the coatings rather differently according to the nature of any subsequently-applied paint. Broadly-speaking it seems that as the proportionate concentration of phosphoric acid relative to the mixed chromium compounds is increased the paint-adhesion properties of the resultant coatings become poorer under some paints, particularly under vinyl paints; yet simultaneously they become enhanced under polyester paints—while conversely, a decrease in the proportionate concentration of phosphoric acid leads to poor paint-adhesion under polyester paints, but somewhat better paint-adhesion under vinyl paints. Since we regard the "universality" of the resultant coatings under both vinyl and polyester paints as a matter of major and perhaps even paramount importance, so as to achieve a compromise between these conflicting requirements which will enable the composition to be effectively used under both vinyl and polyester paints, we greatly prefer and strongly recommend that the phosphoric acid should be present in a ratio by weight of from 3 to 4 of the phosphoric acid (100% H_3PO_4) per 10 parts of the mixed chromium compounds.

Water-soluble polyacrylic acid must be present in the composition if the advantages of the invention are to be achieved. In order to obtain optimum performance and the widest possible "universality" under paint it is however very desirable that it should be present in a relatively low proportionate concentration, namely a ratio by weight of from 4 to 5 parts of water-soluble polyacrylic acid solids per 10 parts of the mixed chromium compounds. We have found it most convenient and generally advantageous to incorporate the water-soluble polyacrylic acid into the composition in the form of an aqueous solution containing substantially 25% by weight of polyacrylic acid solids, such as that commercially-available under the tradename Acrysol A-1.

Acrylic emulsion polymer also must be present in the composition if the advantages of this invention are to be achieved, and for optimum results the proportionate concentration thereof as previously indicated should desirably be rather large, namely at least a ratio by weight of substantially 17 parts of acrylic emulsion polymer per 10 parts of the mixed chromium compounds. On the other hand as the proportionate concentration of acrylic emulsion polymer is raised there are tendencies for the stability of the composition to diminish and for the "universality" of the coating to be impaired, particularly as regards its paint-adhesion properties especially under vinyl paint. Balancing these requirements, we therefore very strongly prefer that the proportionate concentration of acrylic emulsion polymer in the compositions of this invention should lie within the range of from 17 to 20 parts by weight of acrylic emulsion polymer per 10 parts by weight of the mixed chromium compounds.

The acrylic emulsion polymer preferred for use in the compositions of this invention is an emulsion with a non-ionic surfactant containing about 46.0%–47.0% polymer solids with an alkaline pH in the range of 9.0 to 10.0, intended for use in neutral to alkaline applications for forming hard films, such as the commercially-available product known under the tradename Rhoplex AC-73. This differs from Rhoplex AC-200 in that it does not contain any thermosetting components.

It is in fact an unusual aspect of this invention that the otherwise strongly acidic compositions herein disclosed can include an alkaline acrylic emulsion polymer and yet still exhibit stability—and the reason for this is not yet understood with certainty. Nevertheless, we have upon an empirical basis found that it is possible to make highly stable compositions by ensuring that the water-soluble polyacrylic acid has completely interacted with the chromium and/or phosphoric acid before the water-dispersible polymer is added to the other components, and that suspended undissolved particles of reactants are not present in the chromium/polyacrylic acid solution.

The compositions of this invention may be used at a wide variety of dilutions, but it currently appears that they can most conveniently be prepared and marketed in the form of concentrates containing substantially 10 parts by weight of the mixed chromium compounds (calculated as CrO_3) in substantially 200 parts by weight of composition—which however can then be further diluted before use, as will be described hereinafter.

At this point it may be noted that when preparing or diluting the compositions of this invention it is preferred to use either deionized or distilled water, in order to minimize the amount of salts which otherwise might be deposited in the coating and constitute centres of corrosion.

The concentrate just described can be used without dilution, especially for use in applying a coating not intended subsequently to be painted; but when it is intended that the coating formed by the composition shall serve as a foundation for a subsequently-applied siccative finish the concentrate will preferably be diluted before use. As general guidance it may be said that most often the concentrate will be diluted with water to form dilute coating compositions up to 20-times the volume of the concentrate, such compositions thus being made up with water to a total overall weight of from 200 to 4000 parts by weight per 10 parts by weight of the mixed

chromium compounds.

Specific preferred metal-coating compositions for use in accordance with this invention are those having a pH of between 1 and 2, and which contain concentrations, per 200 ml to 4 litres of the resultant aqueous composition, of:

- 5 (i) substantially 8.3 grams of chromium trioxide (of which substantially 46%–50% has been reduced to the trivalent state); 5
 - (ii) substantially 2.9 grams of phosphoric acid (100% H_3PO_4);
 - (iii) substantially 3.8 grams of polyacrylic acid; and
 - 10 (iv) substantially 14.9 grams of acrylic emulsion polymer solids. 10
- According to another aspect of this invention there is therefore also provided a method of preparing a stable aqueous metal-coating composition for coating metal surfaces to enhance their corrosion-resistance and paint-adhesion properties, the coating-forming ingredients of said composition being hexavalent chromium, trivalent chromium, phosphoric acid, polyacrylic acid and an acrylic emulsion polymer; which method comprises the steps of:
- 15 (1) forming an aqueous solution of chromium trioxide and phosphoric acid; 15
 - (2) reducing from 40% to 60% by weight of the hexavalent chromium present in said solution to trivalent chromium under conditions such that substantially all of the reaction products from the reduction remain completely dissolved in the resultant partially-reduced chromium solution;
 - 20 (3) adding polyacrylic acid to the partially-reduced chromium solution under conditions such as to ensure that the reactants present completely interact to form a partially-reduced chromium polyacrylic acid solution; and 20
 - (4) adding acrylic emulsion polymer thereto.
- The preferred characteristics of the various components of the composition are the same in the method of this invention as they are in the composition itself, as previously discussed
- 25 herein. 25
- The reduction is preferably effected by means of a reducing agent that will not form objectionable reaction products in the solution; and that reducing agent will desirably be formaldehyde.
- 30 Generally-speaking, the partial reduction of the hexavalent chromium and the mixing of the polyacrylic acid can be accomplished by techniques essentially the same as those discussed in Schiffman's United States Patent No. 3,185,596, but greater care must be exercised to avoid formation of undissolved residues. One must therefore seek to avoid boil-over during reduction, since that will cause crusts of dried chromium salts to form on the surfaces of the reaction 30
 - 35 vessel, and these redissolve in the chromium-resin solution only with difficulty; hence, the reaction mixture should be maintained during the reduction under conditions that minimize or prevent boil-over. Similarly it is important during the addition of the polyacrylic acid to form a complete solution of all solids present, and it is therefore very desirable to allow the polyacrylic acid-chromium solution to "cure" or "age" for a sufficient time, typically 20 hours or more, to 35
 - 40 ensure that the reaction between the polyacrylic acid and the chromium is complete and that all solids are in solution before the acrylic emulsion polymer is added. The careful introduction of the emulsion to the solution under conditions that minimize "shock" are also beneficial in attaining this objective. 40
- Bearing those various points in mind, a specific preferred method according to this invention
- 45 for preparing a stable aqueous metal-coating composition comprises the steps of: 45
 - (i) dissolving chromium trioxide and phosphoric acid in water in amounts corresponding to substantially 41.5 grams of chromium trioxide and substantially 14.5 grams of phosphoric acid (100% H_3PO_4) per 250–300 ml of water;
 - (ii) adding formaldehyde thereto in an amount corresponding to substantially 4.4 grams of 50 formaldehyde (100% HCHO) per 41.5 grams of the chromium trioxide under such conditions as to prevent boil-over; 50
 - (iii) maintaining the resultant reaction mixture at a temperature within the range of 180°C–190°F (approx. 82°C–88°C) for a period of time at least sufficient to complete the partial reduction of the chromium, to eliminate any unreacted formaldehyde and to ensure the 55 complete dissolution of the resulting reaction products; 55
 - (iv) diluting the resulting solution with from 300 ml to 350 ml of water;
 - (v) adding polyacrylic acid solution thereto in an amount corresponding to substantially 76 grams (25% solids weight/volume) per the original 41.5 grams of chromium trioxide in such a manner as to bring the reaction between the phosphoric acid and mixed chromium compounds 60 on the one hand and the polyacrylic acid on the other hand to completion; 60
 - (vi) adding water so as to bring the total solution volume to substantially 800 ml per original 41.5 grams of chromium trioxide; and
 - (vii) thereafter to the resultant partially-reduced chromium-polyacrylic acid solution adding an acrylic emulsion polymer dispersion in an amount corresponding to substantially 160 grams 65 (containing about 46–47% solids weight/volume) diluted to 200 ml with water per original 65

41.5 grams of chromium trioxide.

The invention of course extends to stable aqueous metal-coating compositions whenever prepared by the method herein described.

According to yet another aspect of this invention there are also provided various processes for using the compositions herein disclosed, whether prepared by the method just described or not.

In one such process, for improving the corrosion-resistance of a metal surface, said metal surface is contacted with the aqueous metal-coating composition herein described and the coating thus formed thereon is thereafter dried and heat-cured.

In another such process, for applying a protective coating to a metal surface, said metal surface is contacted with the aqueous metal-coating composition herein described, the coating thus formed is dried to eliminate water, and thereafter a coating of paint is applied to the thus-treated surface.

Before treatment by the process of this invention the metal surface especially when it is not intended subsequently to paint the coating, should be subjected to conventional precleaning operations to remove dirt, grease and any oxide films and thus promote optimum corrosion-resistance.

The paint applied to the treated surface can with advantage be either a solvent-type paint system or a water-base paint system. While other metals are susceptible to coating by the process of this invention it is above all applicable to the coating of metal surfaces formed of iron, aluminium and/or zinc.

The compositions of this invention can be contacted with the metal surfaces in the manner described in Schiffman's United States Patent No. 3,185,596 or by any other usual application technique known in the art, such as roll-coating, reverse-roll-coating, dip-coating, flow-coating, spray-coating or mist-coating. After the application of the compositions of this invention no rinsing should be required, and there should thus be no waste. Depending of course on the method of application, everything applied to the metal surface should remain there except the water that evaporates off in drying; but should excess amounts be applied, these can be removed by drip, spin or the like, and thus be recovered and reused.

Generally-speaking we have found it desirable to form a coating upon the metal surface which has a coating weight of from 5 to 100 mg/ft² (approx. 0.538–10.76 grams/m²) depending on the metal substrate involved. In underpaint application to iron or aluminium, optimum results are usually obtained with a coating weight of from 5 to 50 mg/ft² (approx. 0.538–5.3 grams/m²) and preferably about 20 mg/ft² (approx. 2.15 grams/m²). In underpaint application to zinc surfaces such as galvanized iron best results are usually obtained with coating weights of 5–50 mg/ft² (approx. 0.538–5.3 grams/m²) and preferably 10–15 mg/ft² (approx. 1.076–1.614 grams/m²). Where unpainted corrosion-resistance is sought, for example on aluminium, that can usually best be obtained with a coating weight of 5–100 mg/ft² (approx. 0.538–10.76 g/m²) and preferably of 80–100 mg/ft² (approx. 8.61–10.76 g/m²).

In order to control the coating weights achieved it is possible empirically to choose and if necessary to vary the concentration of the metal-coating composition employed. For most purposes the concentration of the composition will thus be varied between that of the concentrates herein described (see especially Example 1 hereinafter) and dilutions thereof containing about 0.8% or more solids on a volume/volume basis. At this point it may be noted that dilution is best carried out using deionized or distilled water in order to minimize the amount of salts that would be deposited in the coating the provide points of corrosion. Generally we have found it best to employ the composition in the form of the concentrate according to Example 1 at a 20% dilution in deionized water, prepared by adding four parts of deionized water to one part of the concentrate (volume/volume). When used in this manner, the desired coating thickness is developed faster with less volume and faster dry-off than when applying the known chrome and polyacrylic acid coatings. Moreover, the coatings formed by the process of this invention tend to produce a more uniform surface, which is particularly important for spangled galvanized metal with varied surfaces. Still further, the compositions of this invention generally exhibit better film-forming characteristics than known polyacrylic acid chrome compositions.

The invention of course extends also to metal articles having a surface coated by the process herein described.

In order that the invention shall be more fully understood it will now be described in more detail, though only by way of illustration, with reference to the following examples:—

Example 1—Preparation of Concentrated Composition, suitable for use with or without dilution

41.5 Grams of chromium trioxide were dissolved in about 250–300 ml of deionized water, together with 14.5 grams of phosphoric acid (100% H₃PO₄). The solution was agitated and heated to about 130°F (approx. 55°C) and 4.4 grams of formaldehyde (100% HCHO) were slowly added thereto while stirring over a period of about one hour, the solution being maintained at a temperature between at 185°–195°F (approx. 85°–91°C). After completion

of the addition of the formaldehyde heating was continued for 2 hours, thus maintaining the temperature of the solution at or near boiling. About 300–350 ml of deionized water were then added to the solution, followed by 76 grams of Acrysol A-1 solution (25% solids weight/volume of polyacrylic acid) introduced with stirring. The resulting solution was diluted with deionized water to a volume of about 800 ml, thoroughly mixed and allowed to set and age for 72 hours.

In a separate container, 160 grams of Rhoplex AC-73 acrylic emulsion (46%–47% solids weight/volume) was diluted with sufficient deionized water to make 200 ml total, thus forming a 75% volume/volume "solution". The thus-diluted acrylic emulsion was then slowly added with stirring to the aged partially-reduced chrome-acrylic acid solution prepared as described above.

The resultant concentrate can be used without dilution to form corrosion-resistant coatings upon metals such as iron, zinc and aluminium where it is not intended that a paint should subsequently be applied thereto; or it can be further diluted with deionized water, up to a volume of as much as 20 litres, and then used in under-paint applications.

Example 2—Effect upon Paint-Adhesion and Corrosion-Resistance of the Coating Composition when used under different paint systems

Materials employed:

Test panels were first prepared in the form of clean aluminium panels of 0.024 inch (approx. 0.61 mm) thickness. A metal-coating solution in accordance with the present invention was employed which consisted of the concentrate prepared as described in Example 1 at 20% dilution. For comparison, a conventional metal-coating composition of comparable type was also employed which had been prepared in accordance with the disclosure of Schiffman's United States Patent No. 3,185,596 (hereinafter designated as Formula A), which did not contain any acrylic emulsion polymer.

Technique employed:

Coatings were applied by means of the respective metal-coating compositions to the test panels using the same laboratory spin technique at room temperature, so as to form coatings thereon having a coating weight of about 20 mg/ft² (approx. 0.215 g/m²) in each case. After application of the coating, each panel was dried with hot air using a heat gun, the temperature of the metal during the drying reaching about 110°F to 120°F (approx. 43°–49°C). The panels thus dried were cooled and then painted with standard coil-coating paints, in accordance with the manufacturer's specification in each case, using three different paint systems, as follows:

- a standard single-coat polyester paint system;
- a vinyl paint system; and
- a two-coat Plastisol paint system, using two different primer coat curing temperatures.

Testing procedures:

The painted and cured panels were then subjected to standard tests to determine paint-adhesion and corrosion-resistance, as follows:

- (1) taped reverse-impact adhesion test, carried out at ambient temperature, using a 5/8" ball at 48 inch-lbs (thus an approx. 15.9 mm ball at approx. 6.64 kilogram-metres);
- (2) taped reverse-impact adhesion test, as above but carried out "cold", with the panel at –10°F (approx. –23°C) at the time of impact;
- (3) Cleveland Condensing Humidity Test (ASTM D 714 Rating);
- (4) MEK solvent-resistance test, in which one determines the number of double-wipes with a cheese-cloth soaked with methyl ethyl ketone required to remove paint from the metal surface;
- (5) Pencil Hardness Test.

Results of Testing:

The test results secured from these various testing procedures are summarized in Table I below:

TABLE I

Paint System Employed	Test	Results obtained with:		
		Comparison Conventional Formulation A	Formulation of Example 1 (at 20% dilution)	
5				5
10	a: Standard single-coat Polyester System	Ambient impact	no paint loss	10
		Cold impact	30% paint loss	
		Cleveland Humidity	No. 8 blisters at 72 hours	
15		MEK	57 double rubs	15
		Pencil Hardness	HB	
20	b: Vinyl system	Ambient impact	no paint loss	20
		Cold impact	5% paint loss	
		Cleveland Humidity	No. 8 few blisters at 240 hours	
25		Pencil Hardness	HB	25
		Wet impact*	5% paint loss	
30	c: Two-coat Plastisol Systems	Ambient impact	30% paint loss	30
	—Primer cured at 380 to 390°F (approx 193–199°C)		no paint loss	
35	—Primer cured at 435°F (approx 244°C)	Ambient impact	no paint loss	35
	Two-coat water-based paint	Wet impact*	no paint loss	40
45	[*Note. The "Wet impact" was the same as that of the previously-described ambient impact test, but carried out upon the panel after it had been soaked in deionized water for two hours at room temperature, and impacted immediately upon removal therefrom.]			45

The results set out in Table I above demonstrate that the coatings obtained both in accordance with the present invention and in accordance with the conventional procedures (not containing an acrylic emulsion polymer) when used under a standard single-coat polyester paint system exhibited no paint loss in the taped reverse-impact test at ambient temperatures—but in the cold reverse-impact test there was a 30% paint-loss with the conventional Formulation A, whereas no paint loss was then observed when the under-paint coating had been applied in accordance with the present invention.

Furthermore, the use of conventional Formulation A results in No. 8 blisters after a 72-hour exposure to Cleveland Condensing Humidity; whereas the use of the under-paint coating of the present invention resulted in no blistering even after 240 hours.

In addition, the solvent-resistance obtained using conventional Formulation A (57 double rubs) was unsatisfactory, but that obtained in accordance with the present invention (>100 double rubs) was far better.

Moreover, under the two-coat Plastisol paint system in order to achieve satisfactory quality with respect to the taped reverse-impact adhesion test at ambient temperature it was necessary when using conventional Formulation A to increase the cure temperature of the primer paint, but such an increase was not required when using the coating of the present invention.

Moreover, used under a vinyl paint system, the conventional Formulation A resulted in a 65 pencil hardness of no more than HB, whereas the coating formed in accordance with the present

invention resulted in the required hardness of H to 2H.

Example 3—Effect upon Performance under Various Paint Systems of Changes in the Proportions of Ingredients

- 5 Tests were carried out, generally in the manner described in Example 2 above, using compositions derived from the concentrate of Example 1 modified to show the effects obtained within and without this invention. 5

Composition (i)

- 10 Prepared from 100 ml of the concentrate obtained as described in Example 1, to which there are added 400 ml of a solution in deionized water containing 50 grams of chromium trioxide per litre, thus yielding a test solution which contains a total of 44.3 grams of hexavalent chrome (expressed as CrO_3) per litre and 2.1 grams of trivalent chrome (expressed as chromium) per litre. 10

Composition (ii)

- 15 The composition obtained by diluting the concentrate prepared in Example 1 to 20% dilution while increasing the phosphoric acid concentration from 2.9 g/l to 17.9 g/l. 15

Composition (iii)

- 20 The composition obtained by diluting the concentrate prepared in Example 1 to 20% dilution while increasing the concentration of polyacrylic acid from 3.8 g/l to 18.8 g/l. 20

Composition (iv)

- 25 The composition obtained by increasing the concentration of reduced chrome in the product of Example 1 in the following manner—to 100 ml of that concentrate there are added an additional 400 ml of a solution containing 18.0 g/l of chromium trioxide (partially reduced by the same procedure as that described in Example 1 to an extent of about 47%) so that the total combined solution contains 12.1 g/l of hexavalent chrome (expressed as CrO_3) and 5.5 g/l of trivalent chrome (expressed as chromium). 25

30 Using the same impact and humidity testing procedures as those already described in Example 1 above, the results obtained are summarized in Table II below: 30

TABLE II

Paint System	Test	Results obtained with Composition			
		(i)	(ii)	(iii)	(iv)
40 Polyester	Cold impact	100% paint loss	no paint loss	no paint loss	1 to 2% paint loss
Vinyl	Cold impact	80% paint loss	100% paint loss	90% paint loss	no paint loss
45 "	Ambient impact	5-10% paint loss	30% paint loss	30% paint loss	no paint loss
50 Polyester	Cleveland Humidity (120 hrs.)	No. 4 blisters dense	No. 8 blisters medium dense	No. 2 blisters dense	No blisters
55 Vinyl	Cleveland Humidity (120 hrs.)	No. 8 blisters dense	No. 8 blister few	No. 8 blisters dense	No blisters

The results set out in Table II above illustrate the criticality of the relative proportions between the various ingredients if both "universality" (that is to say usefulness under a variety of different paint systems) and also high performance (as regards both adhesion and corrosion-resistance) are to be achieved. Thus the corrosion-resistance results (as measured by the Cleveland humidity test) under both polyester and vinyl paint systems indicate that the ratio of hexavalent to trivalent chrome is more significant than the total chrome concentration; and it can also be seen that the corrosion resistance decreases upon an increase in the phosphoric acid

or polyacrylic acid concentrations.

CLAIMS

1. An aqueous metal-coating composition for coating metal surfaces to enhance their corrosion-resistance and paint-adhesion properties, which comprises:
 - (a) mixed chromium compounds consisting of a mixture of hexavalent chromium and trivalent chromium formed by reducing from 40% to 60% of the hexavalent chromium to the trivalent state; together with
 - (b) phosphoric acid;
 - (c) polyacrylic acid;
 - (d) acrylic emulsion polymer; and
 - (e) water in an amount at least sufficient to dissolve and/or disperse all the other components therein to form a solution-like composition.
2. A composition as claimed in claim 1, in which the proportion of hexavalent reduced to the trivalent state does not exceed 55%.
3. A composition as claimed in claim 1 or claim 2, in which the proportion of hexavalent chromium reduced to the trivalent state is within the range of from 46% to 50%.
4. A composition as claimed in any of the preceding claims, in which the phosphoric acid is present in a ratio by weight of from 3 to 4 parts of the phosphoric acid (100% H_3PO_4) per 10 parts of the mixed chromium compounds.
5. A composition as claimed in any of the preceding claims, in which the water-soluble polyacrylic acid is present in a ratio by weight of from 4 to 5 parts of water-soluble polyacrylic acid solids per 10 parts of the mixed chromium compounds.
6. A composition as claimed in any of the preceding claims, in which the water-soluble polyacrylic acid is incorporated in the form of an aqueous solution containing substantially 25% by weight of polyacrylic acid solids.
7. A composition as claimed in any of the preceding claims, in which the proportionate concentration of acrylic emulsion polymer lies within the range of from 17 to 20 parts by weight of acrylic emulsion polymer per 10 parts by weight of the mixed chromium compounds.
8. A composition as claimed in any of the preceding claims, in which the acrylic emulsion polymer used is an emulsion with a non-ionic surfactant containing about 46.0%–47.0% polymer solids with an alkaline pH in the range of 9.0 to 10.0.
9. Compositions as claimed in any of the preceding claims, in the form of concentrates containing substantially 10 parts by weight of the mixed chromium compounds (calculated as CrO_3) in substantially 200 parts by weight of composition.
10. Compositions as claimed in any of claims 1 to 8, which comprise the concentrate of claim 9 diluted with deionized water to form a dilute coating composition up to 20-times the volume of that concentrate.
11. Aqueous metal-coating compositions for coating metal surfaces to enhance their corrosion-resistance and paint-adhesion properties, having a pH of between 1 and 2, and which contain concentrations, per 200 ml to 4 litres of the resultant aqueous composition, of:
 - (i) substantially 8.3 grams of chromium trioxide (of which substantially 46%–50% has been reduced to the trivalent state);
 - (ii) substantially 2.9 grams of phosphoric acid (100% H_3PO_4);
 - (iii) substantially 3.8 grams of polyacrylic acid; and
 - (iv) substantially 14.9 grams of acrylic emulsion polymer solids.
12. Compositions as claimed in any of claims 1 to 11 and substantially as herein described.
13. A method of preparing a stable aqueous metal-coating composition, as claimed in any of the preceding claims, for coating metal surfaces to enhance their corrosion-resistance and paint-adhesion properties, the coating-forming ingredients of said composition being hexavalent chromium, trivalent chromium, phosphoric acid, polyacrylic acid and an acrylic emulsion polymer, which method comprises the steps of:
 - (1) forming an aqueous solution of chromium trioxide and phosphoric acid;
 - (2) reducing from 40% to 60% by weight of the hexavalent chromium present in said solution to trivalent chromium under conditions such that substantially all of the reaction products from the reduction remain completely dissolved in the resultant partially-reduced chromium solution;
 - (3) adding polyacrylic acid to the partially-reduced chromium solution under conditions such as to ensure that the reactants present completely interact to form a partially-reduced chromium polyacrylic acid solution; and
 - (4) adding acrylic emulsion polymer thereto.
14. A method as claimed in claim 13, in which the reduction is effected by means of a reducing agent that does not form objectionable reaction products in the solution.
15. A method as claimed in claim 14, in which the reducing agent is formaldehyde.
16. A method of preparing a stable aqueous metal-coating composition, which comprises

the steps of:

- (i) dissolving chromium trioxide and phosphoric acid in water in amounts corresponding to substantially 41.5 grams of chromium trioxide and substantially 14.5 grams of phosphoric acid (100% H_3PO_4) per 250–300 ml of water;
- 5 (ii) adding formaldehyde thereto in an amount corresponding to substantially 4.4 grams of formaldehyde (100% HCHO) per 41.5 grams of the chromium trioxide under such conditions as to prevent boil-over; 5
- (iii) maintaining the resultant reaction mixture at a temperature within the range of 180°C–190°F (approx. 82°C–88°C) for a period of time at least sufficient to complete the
- 10 partial reduction of the chromium, to eliminate any unreacted formaldehyde and to ensure the complete dissolution of the resulting reaction products; 10
- (iv) diluting the resulting solution with from 300 ml to 350 ml of water;
- (v) adding polyacrylic acid solution thereto in an amount corresponding to substantially 76 grams (25% solids weight/volume) per the original 41.5 grams of chromium trioxide in such a
- 15 manner as to bring the reaction between the phosphoric acid and mixed chromium compounds on the one hand and the polyacrylic acid on the other hand to completion; 15
- (vi) adding water so as to bring the total solution volume to substantially 800 ml per original 41.5 grams of chromium trioxide; and
- (vii) thereafter to the resultant partially-reduced chromium-polyacrylic acid solution adding an
- 20 acrylic emulsion polymer dispersion in an amount corresponding to substantially 160 grams (containing about 46–47% solids weight/volume) diluted to 200 ml with water per original 41.5 grams of chromium trioxide. 20
17. A method of preparing a stable aqueous metal-coating composition as claimed in any of claims 13 to 16 and substantially as herein described.
- 25 18. Metal-coating compositions whenever prepared by the method claimed in any of claims 13 to 17. 25
19. A process for improving the corrosion-resistance of a metal surface, in which said metal surface is contacted with an aqueous metal-coating composition as claimed in any of claims 1 to 12 or in claim 18, and the coating thus formed thereon is thereafter dried and heat-cured.
- 30 20. A process for applying a protective coating to a metal surface, in which said metal surface is contacted with an aqueous metal-coating composition as claimed in any of claims 1 to 12 or in claim 18, the coating thus formed is dried to eliminate water, and thereafter a coating of paint is applied to the thus-treated surface. 30
21. A process as claimed in claim 20, in which the paint applied to the coated surface is
- 35 either a solvent-type paint system or a water-base paint system. 35
22. A process as claimed in any of claims 19 to 21, in which the metal surface coated thereby is one formed of iron, aluminium and/or zinc.
23. Metal articles having a surface coated by the process claimed in any of claims 19 to 22.

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